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13. ABSTRACT (Maximum 200 words)

This grant provided funding to making a number of instrumentation upgrades to a 200 keV field-emission Scanning Transmission Electron Microscope (STEM/TEM) at Stevens. This microscope is the centerpiece tool in an ongoing effort supported principally by the Army Research Office to develop and apply novel methods for studying nano and mesoscale structure in both synthetic and natural polymer-based materials using methods of electron energy-loss spectroscopy (EELS). These DURIP-funded enhancements include: (1) a new ccd-based EELS detector (Stevens has the second of these worldwide); (2) enhanced beam scanning coils; (3) an upgraded microscope control and data acquisition system; (4) a light-element X-ray detector.; and (5) a picoammeter Together with funds for cryogenic TEM specimen preparation and manipulation, these enhancements have enabled the Stevens group to assume a world leadership position in the study of beam-sensitive materials structure at sub-20 nm spatial resolution in both dry and frozen-hydrated materials. Among its achievements, the modified tool has been able to map nanoscale water pockets in amphilic polymers at 15 nm resolution. Work is ongoing to study a range of weakly-scattering polymer-based systems using spatially-resolved energy-loss spectroscopy.

14. SUBJECT TERMS
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ARMY RESEARCH OFFICE GRANT DAAD19-00-1-0110

Acquisition of Instrumentation for the High Resolution Study of Polymer Interfaces

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OVERVIEW

This grant provided $171,000 for the purchase of five inter-related pieces of instrumentation for the high resolution study of polymer interfaces by inelastic electron scattering in a field-emission transmission electron microscope (TEM). These pieces of instrumentation either attach directly to or operate in direct support of a Philips field-emission (FEG) CM20 TEM/STEM at the Stevens Institute of Technology. This instrument is the central tool used in research on polymer morphology and polymer interfaces by Professor Matthew Libera. It also supports the materials-development research of at least six other externally-funded research groups on campus as well as research groups at several major area universities.

Libera has a parent grant from the Army Research Office for technique development and application to the study of unstained polymer structure via phase-contrast imaging by transmission electron holography and chemical imaging by energy-loss spectroscopy. Libera also has been supported by an AASERT augmentation grant for work on spatially-resolved electron energy-loss spectroscopy (eels) of the interphase in epoxy-matrix composites. These projects are being pursued in close collaboration with colleagues at the Army Research Laboratory in Aberdeen, MD. Research done using this microscope and the enhancements provided by the DURIP funding has been centrally involved in the training of a number of graduate students who, upon graduation, are bringing increasingly-needed technical skills and experience to both basic and applied research and development groups around the country.

The DURIP funding was highly leveraged. Through grants from NSF, Unilever Research, and EDAX, together with aggressive discounting from EmiSpec, Gatan, and EDAX, additional funding exceeding $326,000 was obtained to execute both the acquisition of instrumentation and their application to problems of scientific relevance.

RESULTS

The DURIP funded purchased five pieces of instrumentation. These are:

1. EmiSpec Vision digital data acquisition and control hardware and software
2. Gatan Enfina high DQE 2-D ccd array detector for the exisiting electron energy-loss spectrometer
3. EDAX ultrathin window EDS X-ray detector
4. Philips high-resolution scan coils upgrade
5. Keithley picoammeter

These tools were ordered, delivered, installed, and accepted over the period 3/99 - 9/00. Their purpose is outlined briefly below.

1. EMiSCAN Vision system : This tool is essential to the quantitative control of the electron beam and the synchronous collection of energy-loss spectra. Among other things, this device creates the controllable digital STEM raster - control of the probe

position, the dwell time at that position, and the interpixel spacing between adjacent sampling positions. The interfaces to the microscope and to the energy-loss spectrometer coupled with real-time data display, manipulation, and processing are daunting. These stymied early attempts by the Stevens group to enter this field using interface tools to be developed in house. Stevens has been fortunate to have a fruitful collaboration with Unilever Research. Unilever purchased an early model of one such system built by EMiSPEC systems. The DURIP-funded upgrade to the modern EmiSpec technology continues to enhyance this collaboration with Unilever, which, for example, was most recently broadened to included an internship opportunity for an American woman, minority graduate student.

2. PEELS spectrometer upgrade: The DQE of the detector used to record any sort of electron-optical image plays a direct role in determining the minimum radiative dose required to collect a certain level of scattered-electron signal. For the majority of polymers, dose must be minimized to limit the structural and chemical damage imparted to the specimen by the incident beam during the measurement process. Tremendous efforts have been made internationally over several decades to minimize damage by cooling or coating a specimen. Depending on the polymer, these approaches can increase the critical dose for catastrophic damage by factors of order 2-5. Upgrading the Stevens PEELS detector to the modern CCD version has permitted experiments using an incident dose approximately 20 times less than previously needed to acquire meaningful signals. This has brought a dramatic advance in Stevens effort to study highly radiation-sensitive materials using this energy-loss spectrometer.

3. Philips high-resolution scan coils: Delivered in January of 1992, the Stevens CM20 FEG TEM/STEM was the first modern FEG instrument Philips installed outside of Europe. As such it was among a few early-generation instruments to highlight necessary design modifications to best exploit its high-brightness field-emission source. Among these was the fact that the resolution in STEM mode was not limited by the size of the focused electron probe as was the case for a traditional LaB_6 source, but rather by current instabilities in the scan coils. The retrofit of high-resolution scan coils has (a) enhanced the ultimate spatial resolution by a factor of about two; and (b) enabled direct access to the scan coils from the EmiSpec Vision thus permitting scanned-probe operation in both TEM and Nanoprobe modes of microscope operation.

4. EDAX R-TEM Ultrathin-window X-ray detector: The Stevens CM20 TEM/STEM was previously equipped with a Be-window X-ray detector. Because of its thickness, a Be-window detector absorbs X-rays from light elements. Typically the lightest element that can be studied using such a detector is Na. The elements B, C, N, and O - essential to studies involving most polymers - cannot be seen. An ultra-thin window (UTW) detector uses a lightly aluminized thin polymer film which is far more transparent to lower energy X-rays and enables the study of elements as light as B. The new ultrathin window detector has enabled X-ray analysis of a variety of light elements relevent to polymers and polymer interfaces. This detector is interfaced to the EmiSpec system for operation and control.

5. Keithley picoammeter: This instrument is essential to the quantitative determination of electron dose in beam-sensitive materials such as polymers. It has been used in conjunction with custom Faraday stages for both the CM20 FEG TEM/STEM of central interest to the present research as well as the LEO 982 FEG SEM within the same laboratory. The latter tool has been used to make quantitative low-energy electron transmission measurements through thin polymer films, a subject relevant to studies of the fundamental physics of energy-deposition mechanisms.

LEVERAGING SUCCESS

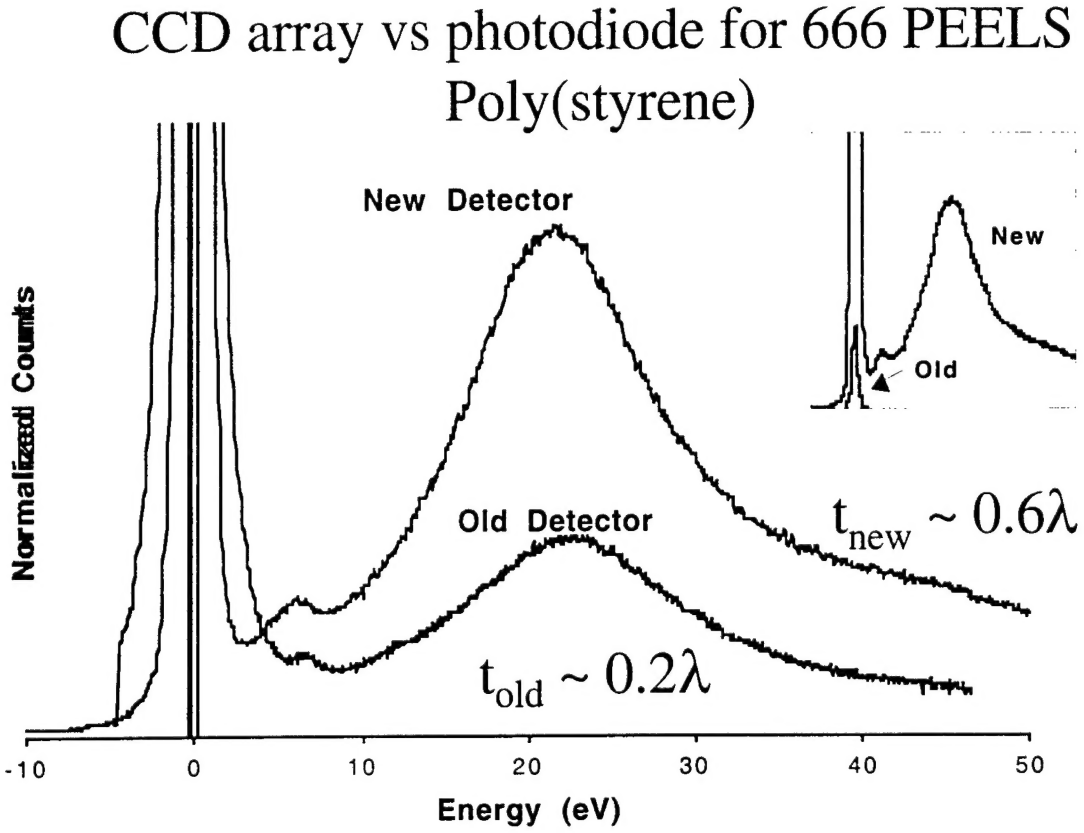
The DURIP funding of $171,00 was leveraged to secure over $326,000 of non-DOD and non-Stevens funding. As part of the instrumentation purchases, manufacturers - Emispec, Gatan, and EDAX - offered substantial discounts to the purchase price. These went far beyond the normal discounting practiced by any of these companies. All were motivated by the fact that the new instrumentation, together with the physical and intellectual infrastructure at Stevens in the area of electron optics, provide excellent beta development platforms for next-generation instrumentation and software. These discounts combine to a match of approximately $105,500. In addition, a second instrumentation grant, submitted after the DURIP proposal submission, was awarded by NSF in the amount of $111,322. These funds were used to purchase instruments specifically to enable the study of frozen hydrated materials using the DURIP instrumentation. Several of these tools were requested within the DURIP proposal but funding was insufficient to purchase them under the DOD program. Finally, grants from EDAX ($25,000; 10/1/99 - 9/31/01) and Unilever Research ($85,000; 1/1/01 - 12/31/01) were awarded to Stevens in direct support of the instrumentation funded by the DURIP grant.

TWO SALIENT RESULTS

This section describes two specific results of significance derived from the DURIP funding. Many others could be presented.

A key enhancement made by the funding was the upgrade of the first-generation energy-loss spectrometer at Stevens. The essential change was that a 2-D ccd array detector was substituted for the original linear photodiode array detector. Figure 1 thus shows energy-loss spectra collected from poly(styrene) using the original detector and the new detector. Based on a t/λ-type determination, the sample thickness in the experiment using the new detector is about three times that in the experiment using the old detector. Nevertheless, the results are absolutely compelling. The main diagram shows spectra normalized to themselves in order to plot them on the same scale. The fact the point spread function of the new detector is substantially better than that of the old detector is obvious from the substantially narrower zero-loss peak. This improvement enables far better resolution of fine structure in both valence and core-loss edges as well as far better removal of zero-loss features from low-loss spectra. The inset shows spectra collected using the new detector and the old detector now plotted

on the same scale. The number of counts in the spectrum collected using the new detector is dramatically higher than that collected using the old detector. This is due to a far higher Detective Quantum Efficiency (DQE). Using the new detector, a count is recorded in the spectrometer for almost every electron incident on the detector. Using the old detector, about 25 electrons were needed to generate count. With the new detector, far less incident dose is thus needed to generate the same level of signal previously generated using the photodiode array.



$I_{\pi-\pi^*}$ = 152,000 counts
$I_{\pi-\pi^*}$ = 598 counts

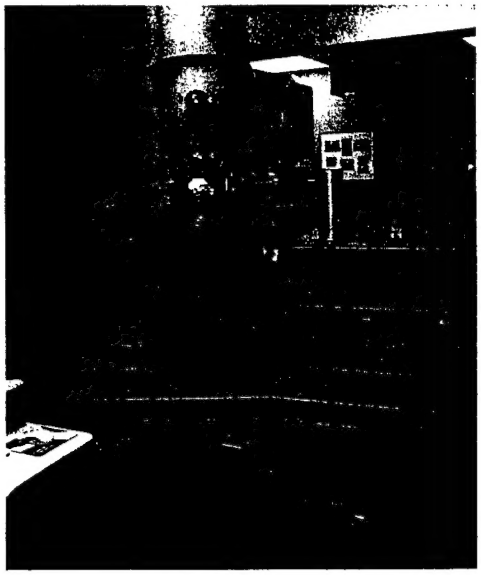


Figure 1 - the new Gatan enfina 2-D ccd energy-loss detector has a substantially narrower point-spread function and a quantum efficiency approximately 25 times that of theprevious linear photodiode array detector.

A principal focus of research using the DURIP-enhanced CM20 is spatially resolved electron energy loss spectroscopy. This technique generates a 3-D dataset. There are two dimensions with the spatial coordinates of x and y typical of any image. The third dimension represents energy loss. Each column in the 3-D dataset coresponds to an entire electron energy-loss spectrum collected from a particular position x-y. Such a dataset contains an extensive amount of information.

Figure 2 shows an image reconstructed from a 3-D spectrum dataset that quantitatively maps water in a specimen of frozen-hydrated biological tissue. Each pixel in the image represents a specimen area of approximately 75 nm x 75 nm. Dark contrast indicates a high concentration of water. Work is ongoing to apply this method to the high resolution study of water in hydrated polymers and at polymer interfaces. The Stevens group is uniquely positioned to do this type of research.

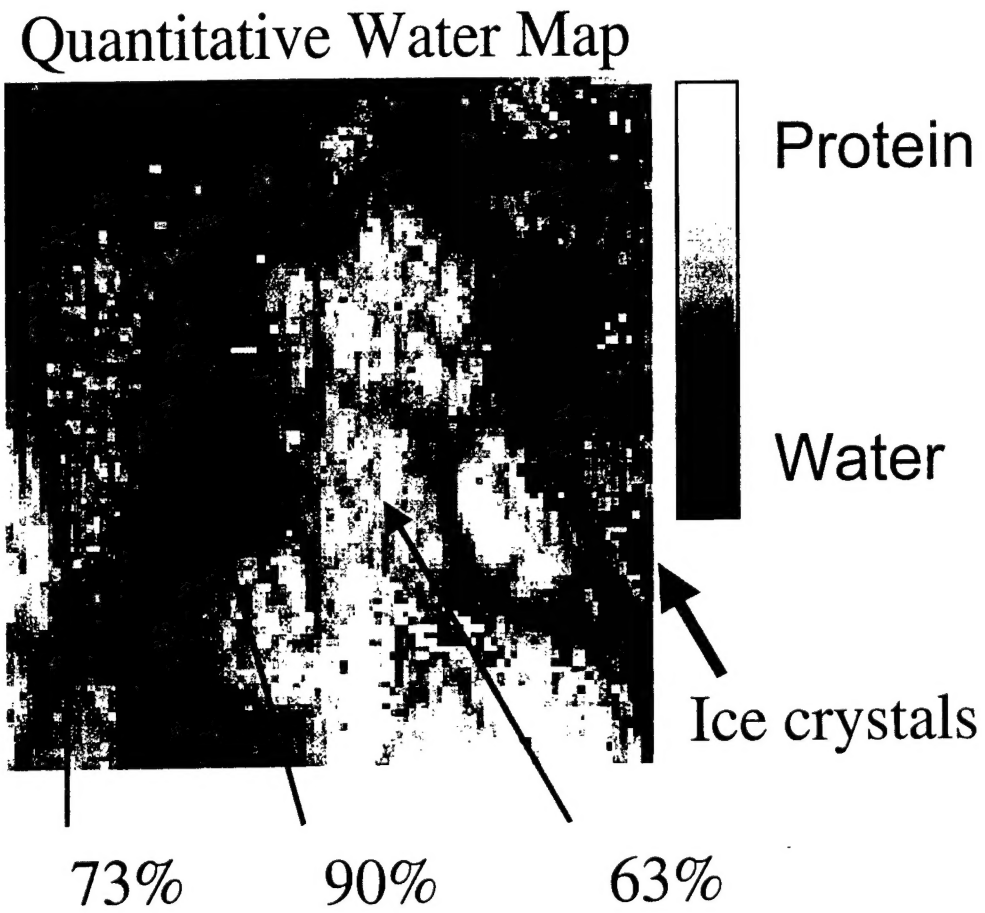


Figure 2 - Spatially resolved map of water concentration in a frozen hydrated section of porcine tissue.

PUBLICATIONS

These were reported within the parent grant reports.

INVITED PRESENTATIONS

The chemical width of polymer interfaces, 12/2/99, Materials Research Society Fall Meeting.

Electron scattering, spectroscopy, and imaging from polymeric solids, 3/17/00, 2-day DOE Workshop on Electron-Driven Processes at Stevens Institute of Technology organized by K. Becker.

Polymer Morphology and the Electron Microscope, Temple University, 11/18/99.

Energy filtering and spectrum imaging of polymers, Annual Meeting of the Microscopy Society of America, 8/14/00.

Dose-limited resolution and new sources of contrast for imaging Polymers, 3-day DOE NTEAM Workshop, Argonne National Laboratory, 7/19/00

Spatially Resolved Electron Scattering from Mesoscopic Polymers, Stevens CBMD Departmental Seminar, 3/1/00

PERSONNEL SUPPORTED

None

AWARDS

None

INVENTIONS

None